o. 87

87

HYDROGEN POTENTIALS OF IXTURES OF ACETIC ACID AND SODIUM ACETATE

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CCXXXIII.—*Hydrogen Potentials of Mixtures of Acetic Acid and Sodium Acetate.*

By George Stanley Walpole.

Mixtures of the type acetic acid–sodium acetate are largely used in certain connexions as "regulator mixtures" in the physico-chemical investigation of protein solutions. During their examination for this purpose their extremely small diffusion potential against saturated potassium chloride was noticed, and the work was, therefore, repeated with a calibrated potentiometer, and every precaution to obtain as high an order of accuracy as possible. It is hoped that these measurements will provide the necessary experimental data for an investigation of the dissociation constant of acetic acid and the dissociation of sodium acetate by the energy method. Some of them have already been used as evidence in the discussion of the vexed question of neutral salt action by McBain and Coleman (this vol., p. 1528). The cells investigated were all of the type:

$$(Pt) \mid H_2, \begin{matrix}\text{acetic acid–sodium acetate} \\ \text{mixture}\end{matrix} \mid \text{saturated KCl} \mid 0{\cdot}10N\text{-KCl}, Hg_2Cl_2 \mid Hg$$

although the actual measurement was made in two stages performed immediately one after the other, as will be explained later. This device in practice was more convenient, and introduced no inaccuracy into the result; rather an increased accuracy was secured thereby.

Two series of mixtures were examined, namely, (1) acetic acid–sodium acetate mixtures in which the total "acetate" was $0{\cdot}20N$, and (2) acetic acid–sodium acetate–sodium chloride mixtures in which the total "acetate" was $0{\cdot}20N$, and the total sodium was $0{\cdot}20N$.

It will be seen at once that each solution of series 1 has a corresponding solution in series 2, which differs from it only in that it contains an amount of sodium chloride molecularly equivalent to the acetic acid present.

Experimental.

The N-acetic acid was standardised by titration (first trace of pink with phenolphthalein) against $0{\cdot}20N$-baryta, which was itself immediately titrated against N-hydrochloric acid.

The N-sodium acetate was made from material which showed no change of properties when an endeavour was made to purify it further by recrystallisation. Each sample gave in normal solution

a trace of colour with two drops of phenolphthalein solution. Samples of this sodium acetate deliberately made acid with acetic acid or alkaline with sodium hydroxide gave on repeated recrystallisation from the best "conductivity" water available, normal solutions of the same properties. Another quantity prepared from pure sodium hydroxide and acetic acid free from higher homologous acids behaved in the same manner. *E.M.F.* measurements against the 0·10*N*-calomel electrode gave 0·7635, and 0·7785, variations which are readily accounted for by 1 part in 5,000 of acetic acid or less. They cannot have any influence on these measurements.

The solutions were first made up to have a refractive index 1·34426 at 17·5° (forty-four scale divisions of Zeiss's dipping refractometer), and then adjusted by an electrometric method devised during the course of this work.

This is referred to in detail on p. 2517. On account of the ready applicability and accuracy of this method, the tedious and less accurate sodium determinations originally employed for the final standardisation were abandoned.

Apparatus.

The electromotive force measurements were made with a potentiometer by Tinsley guaranteed to have a maximum error within 1 in 10,000 at one volt. By means of a compensation arrangement embodied in the instrument measurements of less than 0·18 volt could be read to 0·1 millivolt and estimated to 0·01 millivolt. This could, in most cases, be read with precision, for the zero movement of the electrometer was banished entirely by the complete insulation of the standard cells, the accumulator and the potentiometer from each other, and the whole of the rest of the apparatus. Two cadmium Weston cells were used, one for rough and one for more accurate measurements. The latter at the beginning and at the end of the research was checked against one with a National Physical Laboratory certificate. Its reading on both occasions was 1·0183 ± 0·0001 volt at 20°. In order to observe the movement of the mercury meniscus with precision a cover glass was cemented with Canada balsam to the glass capillary, and a combination of high magnifying power with a micrometer scale employed.

All measurements were made at 18°.

Hydrogen Electrode.

The gas electrode used for the final measurements was of the Brislee type (*Trans. Faraday Soc.*, 1905, **1**, 66). A film of platinum burnt into the surface of Jena-glass was blackened ele

trolytically in the usual manner in a chloroplatinic acid solution containing a little lead acetate, and subsequently treated in accordance with Wilsmore's recommendations. *E.M.F.* readings reproducible and constant to 0·1 millivolt could be readily obtained.

In both series of solutions a preliminary exploration was made using an electrode of a simpler and more convenient type. This electrode depended on the principle discovered by Michaelis (*Biochem. Zeitsch.*, 1909, **18**, 319) that a carefully cleaned and blackened platinum wire saturated with hydrogen and placed in a hydrogen atmosphere so as just to touch the surface of a solution comes into equilibrium with it immediately. The actual form used has been recently described (*Biochem. J.*, 1914, **8**, 131).

It was found that the potentials so obtained differed seldom by more than 1 millivolt from those arrived at subsequently when the more elaborate and more accurate instrument was employed. The hydrogen purified in the usual manner and found to be free from arsenic passed through a Richardson wash flask containing some of the fluid under investigation before entering the hydrogen electrode vessel.

Calomel Electrodes.

Four 0·10*N*-calomel electrodes and four saturated electrodes were prepared at different dates prior to these determinations with the usual precautions. Of the eight calomel half electrodes one of the saturated electrodes (*A*) gave evidence of greater stability of *E.M.F.* than the other seven.

Method of Working.

Since the potential actually measured by the potentiometer is the sum of three potentials, every endeavour was made by suitably devised independent measurements to arrange that these three potentials should be subject to independent examination and criticism. For that reason three sets of measurements were made.

Measurements of E.M.F. *between the* 0·10N-*Calomel Half-electrodes and the Saturated Half-electrode* A.

The saturated half-electrode *A* was chosen as a standard throughout all these measurements because previous experience had shown its stability. This can probably be attributed to the thick bed of crystals of potassium chloride which had settled down on the layer of calomel and to its nine months' previous use. Its actual value, referred to the four 0·10*N*-calomel electrodes prepared, was determined from time to time, and it was checked against one or other of them once or twice a day. There was no evidence that

it varied in value more than 0·10 millivolt in either direction during the course of these measurements.

	May 28.	May 30.	June 2.	June 22.
A—2*C*	0·08834	0·08845	0·08830	0·08836
3*C*	0·08840	0·08860	0·08860	—
4*C*	0·08875	0·08875	0·08870	0·08863
4*C*′.....	0·08855	0·08856	0·08855	0·08865
Mean value	0·08851	0·08859	0·08854	0·08853

The *E.M.F.* of the cell made up of a theoretical 0·10*N*-calomel half-electrode connected to the individual saturated half-electrode (*A*) by means of potassium chloride solution saturated at 18° is therefore taken as 0·0885 volt between the dates May 30th and June 22nd, 1914.

The differences in the electromotive forces given by the different 0·10*N*-calomel electrodes can only be attributed to the fact that they were made up at different times from different samples of mercury, mercurous chloride, and potassium chloride, the purity of which cannot have been absolute in some cases. The figures, although discordant, demonstrate fully that the *E.M.F.* of the saturated half-electrode *A* was throughout these measurements constant. That the value 0·0885 is probably correct within 0·10 millivolt is suggested (1) by the measurement of the hydrogen potential of "standard acetate" (0·6046), which corresponds very closely with that of Sörensen and Koefoed, and Michaelis (0·6045), and (2) by the measurement of the same solution, to be described in a later paper, against a 0·10*N*-calomel electrode of an improved and more accurate type made from specially purified materials (0·60445).

In all the above measurements of "standard acetate" the Bjerrum extrapolation was applied in the usual way.

Measurements of P, *that is, the* E.M.F.'s *of the Cells made up of the Hydrogen Half-electrodes and the Saturated Half-electrode* A, *with Potassium chloride solution saturated at* 18° *as connecting fluid.*

The patterns of hydrogen electrode used have already been described. The connecting fluid was in all cases saturated potassium chloride solution maintained at 18°. On account of the extraordinarily small contact potential between these acetate mixtures and saturated potassium chloride it was not necessary to take precautions to renew the boundary for each observation even in the most accurate determinations. The correction for barometric pressure was applied.

Measurements of the Difference of Contact E.M.F. *at the Boundaries ("Mixture"|1·75N-Potassium Chloride) and ("Mixture"|3·5N-Potassium Chloride) for each Acetic Acid–Acetate Mixture Examined.*

The side-tubes of two saturated electrodes (2*B* and 3*B*) placed adjacently in the same water-bath dipped into two small beakers, one containing 3·5*N*-potassium chloride and the other 1·75*N*-potassium chloride. These solutions were first bridged across with 1·75*N*-potassium chloride solution in a glass tube.

As the cell is symmetrical, the *E.M.F.* should be zero. It was actually about 0·10 millivolt in the usual case. Then, instead of using 1·75*N*-potassium chloride to link across the 1·75*N*- and the 3·5*N*-potassium chloride solutions, the liquid under examination was used, and the second *E.M.F.* reading taken. The difference of these two potentials (*d*), due regard being paid to algebraic sign, was then considered to be the diffusion potential of the solution in question against saturated potassium chloride solution.

At this juncture some remarks may be made about the measurement, in two stages, of the cell indicated diagrammatically in the introduction of this paper. The circumstances which suggested this procedure, and the results in practice, tend to show that if anything the error of measurement was thereby reduced. It certainly was not increased.

In the water-bath was a small vessel of saturated potassium chloride solution, and into it dipped the side-tubes of the saturated electrode *A*, a 0·10*N*-calomel electrode, and the hydrogen electrode containing the fluid under examination. At first three readings were always taken, that is, the hydrogen electrode against each calomel electrode in turn and the calomel electrodes against each other. In the case where the fluid in the hydrogen electrode has a low specific conductivity the first two measurements were fatiguing, and through any minute accidental electrical leakages of the apparatus correspondingly inaccurate. On the other hand, because of the low resistance of the resulting cell and the use of the multiplying shunt in the potentiometer, the measurement of the two calomel electrodes against each other is always of a high order of accuracy. It was therefore quickly discovered that, on account of the accuracy of the potentiometer exceeding that of any measurement made with it, one of the three measurements was superfluous. The direct measurement of the hydrogen electrode potential against the 0·10*N*-calomel electrode was the one discarded because it was that involving the higher resistance; the substitution of the indirect measurement, which in the case of good conducting fluids always

gave identical results, when the 0·10*N*-calomel electrode was corrected for its variation from the mean value of all the 0·10*N*-calomel electrodes, was preferred. Although in many cases the direct measurements against the 0·10*N*-calomel electrode were made with identical results, for the sake of uniformity and simplicity of explanation the results are expressed in the form here given.

Difficulties in Diffusion Potential Measurements.

Weyl (*Diss.*, Karlsruhe, 1905), Lewis and Rupert (*J. Amer. Chem. Soc.*, 1911, **33**, 299), Cumming and Gilchrist (*Trans. Faraday Soc.*, 1913, **9**, 174), Bjerrum (*Zeitsch. Elektrochem.*, 1911, **17**, 58), and others have shown that the difference of potential between the two sides at the boundary of two dissimilar electrolyte solutions depends on the amount of mixing at the boundary and the time for which the boundary has been formed. A convention seems to be established that in order to provide data for comparative measurements these potentials should be measured for a freshly prepared boundary in relation to which no special precautions have been taken to avoid mixing.

The author has found, using the arrangement described on p. 2505, that *E.M.F.* readings varying from 3·5 to 5·5 millivolt could be observed in a few minutes if the two vessels containing 1·75*N*-potassium chloride and 3·5*N*-potassium chloride were linked up by means of a tube containing 0·10*N*-hydrochloric acid. Considerable experiments with this arrangement only led to concordant and consistently reproducible results with 0·10*N*-hydrochloric acid, when, instead of a connecting tube, two tapes were led down, one from each potassium chloride vessel to the opposite sides of a vessel containing 0·10*N*-hydrochloric acid placed at a lower level. It may be that this arrangement is the experimental realisation of the "ideal freshly prepared mixed boundary" of Cumming. As it happens, the diffusion potentials of the two series referred to in the introduction to this paper were so small that the values of d were the same whether glass tubes or tapes were used. On the other hand, some other solutions referred to later—an extension of series 2—gave values for d which could not be fixed with the same order of accuracy, and hence in these cases the values of d (see table III) are printed in italics.

Expression of Results.

It was desired to place on record two *E.M.F.*'s with regard to each solution examined:

(1) The *E.M.F.* (V) of the cell:

$$\mathrm{Pt} \mid \mathrm{H_2},\ \text{"solution"} \mid \text{saturated KCl} \mid 0{\cdot}10N\text{-KCl}, \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}$$

(2) The *E.M.F.* (E) being the potential of the hypothetical cell:

$$\mathrm{Pt} \mid \mathrm{H_2},\ \text{"solution,"}\ 0{\cdot}10N\text{-KCl}, \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}.$$

from which the contact potential at the boundary of the "solution" and $0{\cdot}10N$-potassium chloride has been eliminated by Bjerrum's extrapolation method (*Zeitsch. Elektrochem.*, 1911, **17**, 389).

A consideration of the cells indicated below will show at once that:

$$V = P + 0{\cdot}0885 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$E = P + 0{\cdot}0885 - d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is assumed that no difference of potential exists between any two of the three solutions: $1{\cdot}75N$-potassium chloride, $3{\cdot}5N$-potassium chloride, and potassium chloride solution saturated at 18° ($4{\cdot}1N$), and that the small unknown difference of potential between $0{\cdot}10N$-potassium chloride and any one of these solutions is a constant value x, a quantity which it will be seen cancels out in both equations above:

(1) $\overset{W}{\mathrm{Pt}} \mid \mathrm{H_2},\ \text{"solution"} \overset{y'}{\mid}$ saturated KCl, $\mathrm{Hg_2Cl_2} \overset{-X}{\mid} \mathrm{Hg}$. $E.M.F. = P.$

(2) $\overset{X}{\mathrm{Hg}} \mid \mathrm{Hg_2Cl_2}$, saturated KCl $\overset{x}{\mid}$ $0{\cdot}10N$-KCl, $\mathrm{Hg_2Cl_2} \overset{-Y}{\mid} \mathrm{Hg}$. $E.M.F. = f.$

(3) $\overset{X}{\mathrm{Hg}} \mid \mathrm{Hg_2Cl_2}$, saturated KCl $\overset{O}{\mid}$ $3{\cdot}5N$-KCl $\overset{-y'}{\mid}$ "solution" $\overset{y}{\mid}$ $1{\cdot}75N$-KCl $\overset{O}{\mid}$ saturated KCl, $\mathrm{Hg_2Cl_2} \overset{-X}{\mid} \mathrm{Hg}$. $E.M.F. = d.$

(4) $\overset{W}{\mathrm{Pt}} \mid \mathrm{H_2},\ \text{"solution"} \overset{y}{\mid}$ $1{\cdot}75N$-KCl $\overset{x}{\mid}$ $0{\cdot}10N$-KCl, $\mathrm{H_2Cl_2} \overset{-Y}{\mid} \mathrm{Hg}$. $E.M.F. = B.$

(5) $\overset{W}{\mathrm{Pt}} \mid \mathrm{H_2},\ \text{"solution"} \overset{y'}{\mid}$ $3{\cdot}50N$-KCl $\overset{x}{\mid}$ $0{\cdot}10N$-KCl, $\mathrm{Hg_2Cl_2} \overset{-Y}{\mid} \mathrm{Hg}$. $E.M.F. = B'.$

(6) $\overset{W}{\mathrm{Pt}} \mid \mathrm{H_2},\ \text{"solution"} \mid$ saturated KCl $\mid$ $0{\cdot}01N$-KCl, $\mathrm{Hg_2Cl_2} \overset{-Y}{\mid} \mathrm{Hg}$. $E.M.F. = V.$

(7) $\mathrm{Pt} \mid \mathrm{H_2},\ \text{"solution,"}\ 0{\cdot}10N\text{-KCl} \mid \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}$ (hypothetical cell). $E.M.F. = E.$

The *E.M.F.* (E) of the hypothetical cell No. 7 above, according to Bjerrum's extrapolation method, is $2B' - B$:

$$E = 2B' - B$$
$$= W - Y + 2y' + x - y.$$

Also from the equations above:

$$-(P + f - d) = W - Y + 2y' + x - y;$$

therefore $E = P + f - d,$

$$= P + 0{\cdot}0885 - d.$$

That is to say, equations (1) and (2) hold, and the method of employing Bjerrum's extrapolation method used in these measurements can differ in no way, in the actual result reached, from that of Sörensen and other workers.

Series I.

Acetic Acid–Sodium Acetate Mixtures: Total "Acetate" is 0·20 Normal.

In order to prepare each solution n c.c. of N-acetic acid and $(20-n)$ c.c. of N-sodium acetate were mixed and diluted to 100 c.c. Where n or $(20-n)$ was small, suitable precautions were taken to measure the volumes accurately. A comparatively large volume of the normal solution was diluted ten- or one hundred-fold, and ten or one hundred times this volume taken. The results of the measurements of V and d for these solutions are given in table I. Figures in brackets are obtained by extrapolation on accurately squared paper. Where more than one measurement is given the results are from different preparations of N-sodium acetate and N-acetic acid on different dates. The particular mixture 10 c.c. of N-acetic acid + 10 c.c. of N-sodium acetate diluted to 100 c.c.—"standard acetate"—was measured whenever an electrode was re-blackened or new standard solutions were prepared. The consistent result $(P+0{\cdot}0885)=0{\cdot}6047$, which when corrected for diffusion potential becomes 0·6046, is in good accord with the corrected result 0·6045, which is the result for the same mixture as determined by Sörensen and Koefoed and by Michaelis. The frequent repetition of this determination was adopted as an additional safeguard against the errors which are apt to enter into determinations of this kind.

According to the theory of mass action applied to the feebly dissociated acetic acid the relationship

$$[\mathrm{H}^{\cdot}]=\frac{k_a\mathrm{C}}{\alpha\mathrm{C}'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

should hold; and it is interesting to examine over what range of ratios of acetic acid and sodium acetate the hydrogen potentials against the 0·10N-calomel electrode may be calculated.

To do this the right hand expression of (3) is substituted into the well-known energy equation:

$$E.M.F.=\epsilon_h+\frac{RT}{F}\log_n\frac{1}{[\mathrm{H}^{\cdot}]} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$=0{\cdot}3377-0{\cdot}0577\log_{10}\left(\frac{k_a\mathrm{C}}{\alpha\mathrm{C}'}\right) \quad . \quad . \quad . \quad . \quad (5)$$

For calculating α Kohlrausch's conductivity measurements may be used, and $18{\cdot}83\cdot10^{-6}$* may be taken as the dissociation constant of acetic acid at 18°. Sörensen's value for ϵ_h at 18° has been

* This is a purely arbitrary value chosen so that the calculated *E.M.F.* for "standard acetate" will agree with the observed value.

TABLE I.

C. Concentration of acetic acid.	C' Concentration of sodium acetate.	$V=(P+0{\cdot}0885)$ small electrode.	$V=(P+0{\cdot}0885)$ large and more accurate electrode.	d.	$E=(P+0{\cdot}0885-d)$.	μ (Kohlrausch) $\mu_\infty=76{\cdot}8$.	$E=(P+0{\cdot}0885-d)$ (calculated by equation 5).	Difference between calculated and experimentally determined values of E.	$[H^+]$	P_H^+.
$0{\cdot}00008N$	$0{\cdot}19992N$	0·7635	0·7785	0·00015	—	57·1	0·8395	—	—	—
0·0002	0·1998	—	—	(„)	—	57·1	0·7769	—	—	—
0·0005	0·1995	—	—	(„)	—	(57·2)	0·7531	—	—	—
0·001	0·199	—	—	(„)	—	(57·2)	0·7383	—	—	—
0·0025	0·1975	—	0·7140	(„)	0·7138	(57·2)	0·7125	0·0013	$3{\cdot}03.10^{-7}$	6·518
0·005	0·195	—	0·6963	(„)	0·6961	(57·3)	0·6948	0·0013	$6{\cdot}15.10^{-7}$	6·211
0·0075	0·1925	—	0·6855	(„)	0·6853	(57·4)	0·6844	0·0009	$9{\cdot}46.10^{-7}$	6·024
0·01	0·19	—	0·6780 0·6783	(„)	0·6778	(57·5)	0·6768	0·0010	$1{\cdot}28.10^{-6}$	5·894
0·02	0·18	—	0·6595	(„)	0·6593	(57·9)	0·6582	0·0011	$2{\cdot}67.10^{-6}$	5·574
0·03	0·17	0·6475	0·6479	(0·00013)	0·6478	(58·3)	0·6470	0·0008	$4{\cdot}23.10^{-6}$	5·374
0·04	0·16	—	0·6394	0·00013	0·6393	(58·65)	0·6383	0·0010	$5{\cdot}93.10^{-6}$	5·227
0·05	0·15	0·6317	—	(„)	0·6316	(59·0)	0·6313	0·0003	$8{\cdot}07.10^{-6}$	5·093
0·06	0·14	—	0·6257	(„)	0·6256	(59·45)	0·6251	0·0005	$1{\cdot}02.10^{-5}$	4·990
0·08	0·12	0·6136 0·6137	0·6149	0·0001	0·6148	(60·25)	0·6144	0·0004	$1{\cdot}58.10^{-5}$	4·802
0·10	0·10	0·6047 0·6047 0·6047	0·6047 0·6047	0·0001	0·6046	61·1	0·6046	0·0000	$2{\cdot}37.10^{-5}$	4·626

TABLE I (*continued*).

C. Concentration of acetic acid.	C' Concentration of sodium acetate.	$V=$ ($P+0{\cdot}0885$) small electrode.	$V=$ ($P+0{\cdot}0885$) large and more accurate electrode.	d.	$E=$ ($P+$ 0·0885-d).	μ (Kohlrausch) $\mu_\infty=$ 76·8.	$E=$ ($P+$ 0·0885$-d$) (calculated by equation 5).	Difference between calculated and experimentally determined values of E.	[H·].	P_H^+.
0·12	0·08	0·5937 0·5939	0·5947	0·00005	**0·5947**	(62·0)	0·5948	−0·0001	$3{\cdot}52.10^{-5}$	4·454
0·14	0·06	0·5832 0·5837	**0·5841**	0·00005	**0.5841**	(63·4)	0·5842	−0·0001	$5{\cdot}37.10^{-5}$	4·27
0·16	0·04	0·5707 0·5708	0·(5712)	0·00005	**0(·5712)**	65·12	0·5714	−0·0002	$8{\cdot}97.10^{-5}$	4·047
0·18	0·02	0·5521	0·5525	(„)	**0·5525**	67·9	0·5522	+0·0003	$1{\cdot}89.10^{-4}$	3·723
0·185	0·015	0·5450	—	(„)	**0·5450**	(69·0)	0·5447	+0·0003	$2{\cdot}56.10^{-4}$	3·592
0·190	0·010	0·5348	—	(„)	**0·5348**	70·2	0·5343	0·0005	$3{\cdot}84.10^{-4}$	3·416
0·192	0·008	—	0·5290	(„)	**0·5290**	(71·05)	0·5288	0·0002	$4{\cdot}84.10^{-4}$	3·315
0·194	0·006	0·5225	—	(„)	**0·5225**	(71·95)	0·5216	0·0009	$6{\cdot}28.10^{-4}$	3·202
0·195	0·005	0·5193	—	(„)	**0·5193**	72·4	0·5170	0·0023	$7{\cdot}13.10^{-4}$	3·147
0·196	0·004	0·5155	—	(„)	**0·5155**	72·95	0·5115	0·0040	$8{\cdot}30.10^{-4}$	3·081
0·197	0·003	—	0·5105	(„)	**0·5105**	73·55	0·5044	0·0061	$1{\cdot}01.10^{-3}$	2·994
0·198	0·002	—	0·5057	(„)	**0·5057**	74·3	0·4943	0·0114	$1{\cdot}23.10^{-3}$	2·912
0·199	0·001	—	0·4995	(„)	**0·4995**	75·2	0·4771	0·0224	$1{\cdot}57.10^{-3}$	2·804
0·200	0·000	0·4934	0·4932 0·4932	0·0001	**0·4931**	—	—	—	$2{\cdot}01.10^{-3}$	2·696

adopted. The results calculated according to this equation are given in column 8 of table I. The difference between the observed values and the calculated values is given in the next column. It must not be considered that these are errors in potential determinations. Their theoretical significance is connected with those problems in connexion with which these measurements were undertaken. As a matter of interest it may be here recorded that in series I the values of E for those solutions of composition between

C.	C'.	Ratio C/C'.	[H·]	P_H^+.	E.
0·0075N	0·1925	0·039	$9·46 \times 10^{-7}$	6·024	0·6844
0·1940N	0·0060	32·3	$6·28 \times 10^{-4}$	3·202	0·5216

may be calculated with an error not exceeding one millivolt from equation (4) above.

In columns 10 and 11 are calculated, from the observed *E.M.F.*'s corrected for diffusion potential, the hydrion concentrations and the hydrogen-ion coefficient (P_H^+) on the basis $\epsilon_h = 0·3377$ and $K = 0·0577$.

With regard to the value of E for pure sodium acetate it has been calculated on the basis of 0·008 per cent. of hydrolysis (compare Walker, *Zeitsch. physikal. Chem.*, 1900, **32**, 138). The large difference between the experimentally determined values of E for the two samples of pure sodium acetate examined has been already discussed (p. 2502). The discrepancy between these determinations and the calculated value of E may be attributed to similar causes.

At the other end of the series the divergence between the calculated and observed values when the ratio C/C′ exceeds 32·3 may at once be attributed to the incorrectness of one of the original assumptions in this case. The total [Ac′] concentration in such solutions is no longer represented with sufficient approximation by $\alpha C'$.

The magnitude of the differences in column 9 of table I suggests the search for an expression which will represent still more accurately the relationship between the hydrion concentration [H·] and the composition of these acetic acid–sodium acetate mixtures.

We may write first of all

$$[H^{\cdot}] = \frac{k_a[HAc]}{[Ac']}.$$

Instead of [HAc], the concentration of the undissociated acetic acid, may be substituted (C − [H·]); and, as an attempt at expressing [Ac′] in terms of α, C′, and [H·], the relationship

$$[Ac'] = \alpha' C' + [H^{\cdot}]$$

where α' is the value α applied, now to C′ (the concentration of sodium acetate) as before, but, in accordance with Ostwald's isohydric principle to the acetic-ion concentration [Ac′].

The completed formula is therefore

$$[H^{\cdot}] = \frac{k_a(C - [H^{\cdot}])}{\mu_{[Ac']}/\mu_{\infty} C' + [H^{\cdot}]} \quad \ldots\ldots \quad (6)$$

The solution of this equation for $[H^{\cdot}]$ does not give a simple expression, and, as $[H^{\cdot}]$ is a small quantity, its occurrence in the numerator and denominator of this expression is more conveniently left undisturbed, and the calculation performed by the method of trial and error.

In this way the value of $[H^{\cdot}]$ is found, which, when substituted into the expression $\frac{\mu_{\infty}}{C'}\left(\frac{k_a(C - [H^{\cdot}])}{[H^{\cdot}]} - [H^{\cdot}]\right)$ gives a. result $\mu_{[Ac']}$, which is equal to the value of μ corresponding with a sodium acetate concentration of $\left(\frac{k_a(C - [H^{\cdot}])}{[H^{\cdot}]}\right)$ in Kohlrausch's tables.

From the values of $[H^{\cdot}]$ so calculated the values of E are obtained by means of equation (4).

Examination of equations (3) and (6) shows that when $C' = 0$ the former becomes indeterminate, but the latter simplifies to the equation:

$$[H^{\cdot}] = \sqrt{k_a(C - H^{\cdot})}$$

Table II.

C= concentration of acetic acid.	E=observed *E.M.F.* against decinormal electrodes corrected for diffusion potential.	E calculated by equations (6) and (4) above.	Difference between calculated and observed values.
0·0025	0·7138	0·7132	+0·0006
0·005	0·6961	0·6955	+0·0006
0·0075	0·6853	0·6851	+0·0002
0·01	0·6778	0·6776	+0·0002
0·02	0·6593	0·6590	+0·0003
0·03	0·6478	0·6475	+0·0003
0·04	0·6393	0·6389	+0·0004
0·05	0·6316	0·6318	−0·0002
0·06	0·6256	0·6256	0·0000
0·08	0·6148	0·6148	0·0000
0·10	0·6046	0·6050	−0·0004
0·12	0·5947	0·5953	−0·0006
0·14	0·5841	0·5846	−0·0005
0·16	0·5712	0·5718	−0·0006
0·18	0·5525	0·5526	−0·0001
0·185	0·5450	0·5455	−0·0005
0·190	0·5348	0·5354	−0·0006
0·192	0·5290	0·5303	−0·0013
0·194	0·5225	0·5240	−0·0015
0·195	0·5193	0·5204	−0·0011
0·196	0·5155	0·5163	−0·0008
0·197	0·5105	0·5117	−0·0012
0·198	0·5057	0·5062	−0·0005
0·199	0·4995	0·5005	−0·0010
0·200	0·4931	0·4943	−0·0012

which is the expression for the hydrion concentration of an acetic acid solution of concentration C.

The results of using equations (4) and (6) for calculating the hydrogen potentials of acetic acid–sodium acetate mixtures against the 0·10*N*-calomel electrode are given in column 3 of table II. C′ is, of course, (0·20 − C), and the values of k_a ($18{\cdot}83 \times 10^{-6}$), Kohlrausch's values for α, and the constants are taken as before.

An expression based on the law of mass action has, therefore, been found, by which the *E.M.F.*'s of the "0·20*N*-total acetate" series of acetic acid–sodium acetate mixtures may be calculated accurately. The observed values for the series from $C/C' = \infty$ to $C/C' = 0{\cdot}039$ differed from the calculated values by a maximum of 1·5 millivolt in a single instance.

It is not possible at present to go yet further and investigate the significance of these differences and their gradual change of sign as we pass from one end of the series to the other, for the uncertainty of the dissociation of sodium acetate at different dilutions is greater than the calculated discrepancies.

Series II.

Acetic Acid–Sodium Acetate–Sodium Chloride Mixtures: Total Acetate 0·20 *Normal, Total Sodium* 0·20 *Normal.*

Each solution was prepared by adding m c.c. of *N*-hydrochloric acid to 20 c.c. of *N*-sodium acetate, and diluting the mixture to 100 c.c.

The results are given in table III, which, since it is arranged in a similar fashion to table I, needs little further explanation. In column 1 are given the values of m, and in columns 2, 3, 4, 5 the compositions of the resulting mixtures in terms of acetic acid, sodium acetate, sodium chloride, and hydrochloric acid.

It will be shown later that some of these mixtures would give inaccurate results if prepared in this way. In the region of "20 c.c. *N*-hydrochloric acid + 20 c.c. *N*-sodium acetate" they were prepared by mixing *N*-acetic acid and *N*-sodium chloride with either *N*-hydrochloric acid or *N*-sodium acetate in the right proportions. The greatly increased accuracy of this method of procedure will be clear from the explanation on p. 2517.

As a check on the purity of the reagents and the accuracy of their standardisation, not only this part of the series, but the whole of the determinations were repeated, from $m = 0{\cdot}4$ to $m = 22$, three or four times with the solutions prepared in different manners from the various possible constituents, sodium hydroxide, acetic acid, sodium acetate, hydrochloric acid, and sodium chloride. The

Table III.

m.	C. Concentration of acetic acid.	C'. Concentration of sodium acetate.	Concentration of sodium chloride.	Concentration of hydrochloric acid.	$P+0{\cdot}0885$.	d.	$P+0{\cdot}0885-d$.	[H·].	P_H^+.
0·40	0·004	0·196	0·004	Nil.	0·7017	0·00016	0·7015	$4{\cdot}95.10^{-7}$	6·31
1·05	0·0105	0·1895	0·0105	,,	0·6763	(0·00012)	0·6762	$1{\cdot}36.10^{-6}$	5·87
4·00	0·04	0·16	0·04	,,	0·6375	0·00005	0·6375	$6{\cdot}38.10^{-6}$	5·20
6·00	0·06	0·14	0·06	,,	0·6235	(0·00000)	0·6235	$1{\cdot}11.10^{-5}$	4·95
8·00	0·08	0·12	0·08	,,	0·6125	0·00007	0·6126	$1{\cdot}72.10^{-5}$	4·76
10·00	0·10	0·10	0·10	,,	0·6017	(−0·00016)	**0·6019**	$2{\cdot}64.10^{-5}$	4·58
12·00	0·12	0·08	0·12	,,	0·5905	−0·00025	0·5908	$4{\cdot}11.10^{-5}$	4·39
14·00	0·14	0·06	0·14	,,	0·5790	(−0·00029)	0·5793	$6{\cdot}50.10^{-5}$	4·19
16·00	0·16	0·04	0·16	,,	0·5651	−0·00033	0·5654	$1{\cdot}42.10^{-4}$	3·95
17·00	0·17	0·03	0·17	,,	0·5560	(−0·00036)	0·5564	$1{\cdot}62.10^{-4}$	3·79
18·00	0·18	0·02	0·18	,,	0·5457	−0·00038	0·5461	$2{\cdot}44.10^{-4}$	3·61
18·50	0·185	0·015	0·185	,,	0·5385	(−0·00037)	0·5389	$3{\cdot}26.10^{-4}$	3·49
18·90	0·189	0·011	0·189	,,	0·5293	(−0·00036)	0·5297	$4{\cdot}71.10^{-4}$	3·33
19·00	0·190	0·010	0·190	,,	0·5270	(−0·00036)	0·5274	$5{\cdot}15.10^{-4}$	3·29
19·40	0·194	0·006	0·194	,,	0·5155	(−0·00036)	0·5159	$8{\cdot}17.10^{-4}$	3·09
19·50	0·195	0·005	0·195	,,	0·5125	(−0·00035)	0·5129	$9{\cdot}20.10^{-4}$	3·04
19·90	0·199	0·001	0·199	,,	0·4945	(−0·00035)	0·4949	$1{\cdot}89.10^{-3}$	2·72
20·00	0·200	0·000	0·200	,,	0·4898	−0·00035	**0·4902**	$2{\cdot}27.10^{-3}$	2·64
20·39	0·2000	nil	0·200	0·0039	0·4712	(−0·00023)	0·4715	$4{\cdot}80.10^{-3}$	2·32
20·89	0·2000	,,	0·200	0·0089	0·4549	−0·00006	0·4550	$9{\cdot}27.10^{-3}$	2·03
21·00	0·2000	,,	0·200	0·0100	0·4525	−0·00002	0·4525	$1{\cdot}03.10^{-2}$	1·99
21·40	0·2000	,,	0·200	0·0140	0·4443	0·00010	0·4442	$1{\cdot}43.10^{-2}$	1·85
21·90	0·2000	,,	0·200	0·0190	0·4375	0·00028	0·4372	$1{\cdot}89.10^{-2}$	1·72
22·00	0·2000	,,	0·200	0·0200	0·4365	0·00030	0·4362	$1{\cdot}96.10^{-2}$	1·71
24·00	0·200	,,	0·200	0·0400	*0·4205*	*0·0011*	*0·4194*	$3{\cdot}84.10^{-2}$	*1·42*
26·00	0·200	,,	0·200	0·0600	*0·4105*	*(0·0015)*	*0·4090*	$5{\cdot}81.10^{-2}$	*1.24*
28·00	0·200	,,	0·200	0·0800	*0·4025*	*0·0018*	*0·4007*	$8{\cdot}09.10^{-2}$	*1·09*
32·00	0·200	,,	0·200	0·1200	*0·3935*	*0·0031*	*0·3904*	$1{\cdot}22.10^{-1}$	*0·91*
36·00	0·200	,,	0·200	0·1600	*0·3850*	*(0·0038)*	*0·3812*	$1{\cdot}76.10^{-1}$	*0·75*
40·00	0·200	,,	0·200	0·200	*0·3795*	*0·0045*	*0·3750*	$2{\cdot}26.10^{-1}$	*0·65*

results were consistent to within a millivolt or two. With increasing experience the discrepancies between different *E.M.F.* determinations with the same solution prepared from different materials became less. This constant repetition was made possible by the use of the smaller and more rapidly working type of electrode. The main points were afterwards checked by the larger and more accurate electrode. The *E.M.F.* measurements at these points are in heavier type. They have been utilised by McBain (*loc. cit.*) in support of his views on neutral salt action. He points out that of the 2·9 millivolt difference of hydrogen potential resulting from the addition of 0·20*N*-sodium chloride to 0·20*N*-acetic acid either 1·1 or 1·6 millivolts is accounted for on the principle of isohydrism, depending on the dissociation data assumed for hydrochloric acid. This would leave a small but definite increase in acidity of 1·8 or 1·3 millivolts to be ascribed to an enhancement of the dissociation constant of acetic acid by the sodium chloride.

At other points the series, although carefully examined, may have one or two errors up to ±1·0 millivolt, and cannot claim the higher order of accuracy pertaining to series I, which was investigated later. Those results placed in italics were obtained at the commencement of this investigation, and, unfortunately, through lack of time, it was impossible to check them afterwards. They may possibly be incorrect by several millivolts. The diffusion potentials for these determinations are also open to suspicion. I have included them solely because it is of interest to trace the course of the curve complete from $m=0$ to $m=40$.

Diagrammatic Representation of Results in Series I and II (Fig. 1).

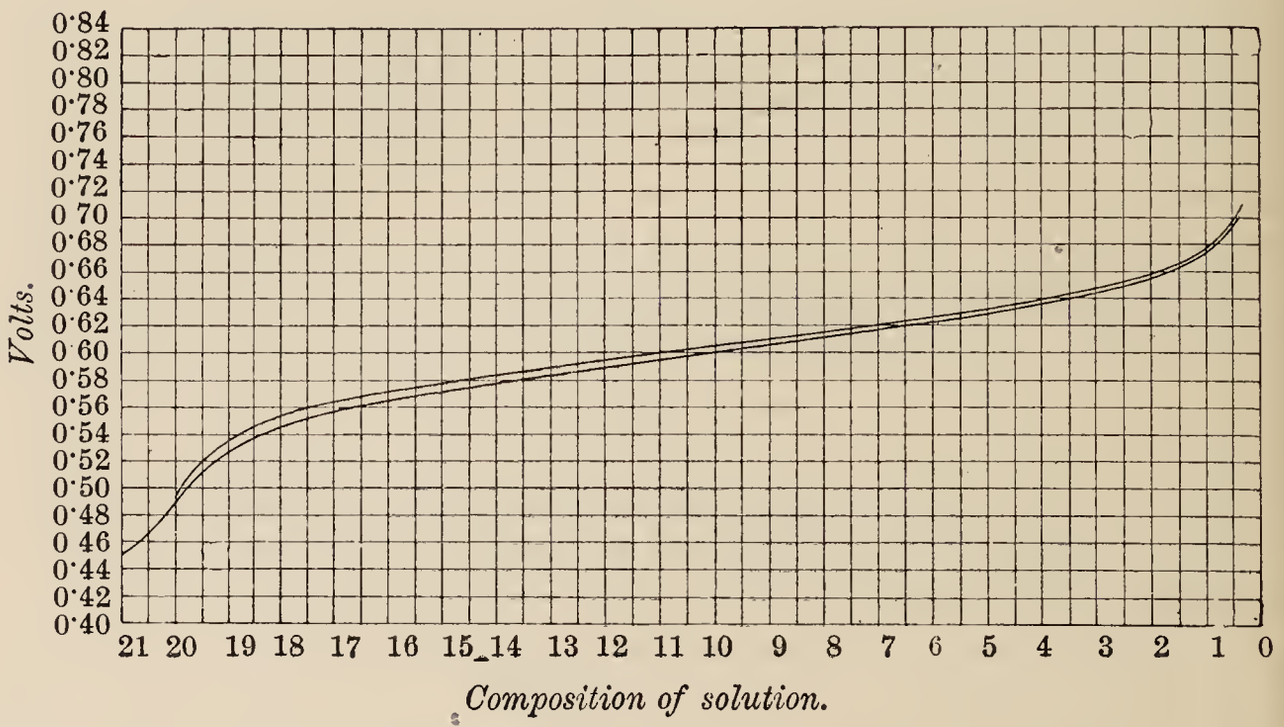
In Fig. 1 are shown two curves, of which the upper one expresses the relationship between the figures in columns 1 and 6 in table I. The curve connecting the calculated values in column 3 of table II and the values of C in column 1 of the same table lies so closely on this curve that in the reproduction it cannot be seen. The lower one expresses the relationship between the c.c.'s of *N*-hydrochloric acid (m) added to 20 c.c. of *N*-sodium acetate, the mixture subsequently being diluted to 100 c.c., and the fully corrected potential against the 0·10*N*-calomel electrode of a hydrogen electrode in equilibrium with the diluted solution (see table III).

The Effect of Twenty-fold Dilution on the Hydrogen Potential of Solutions in Series I and II.

Except in the cases of pure sodium acetate and mixtures containing only traces of acetic acid, the hydrogen potential of all the

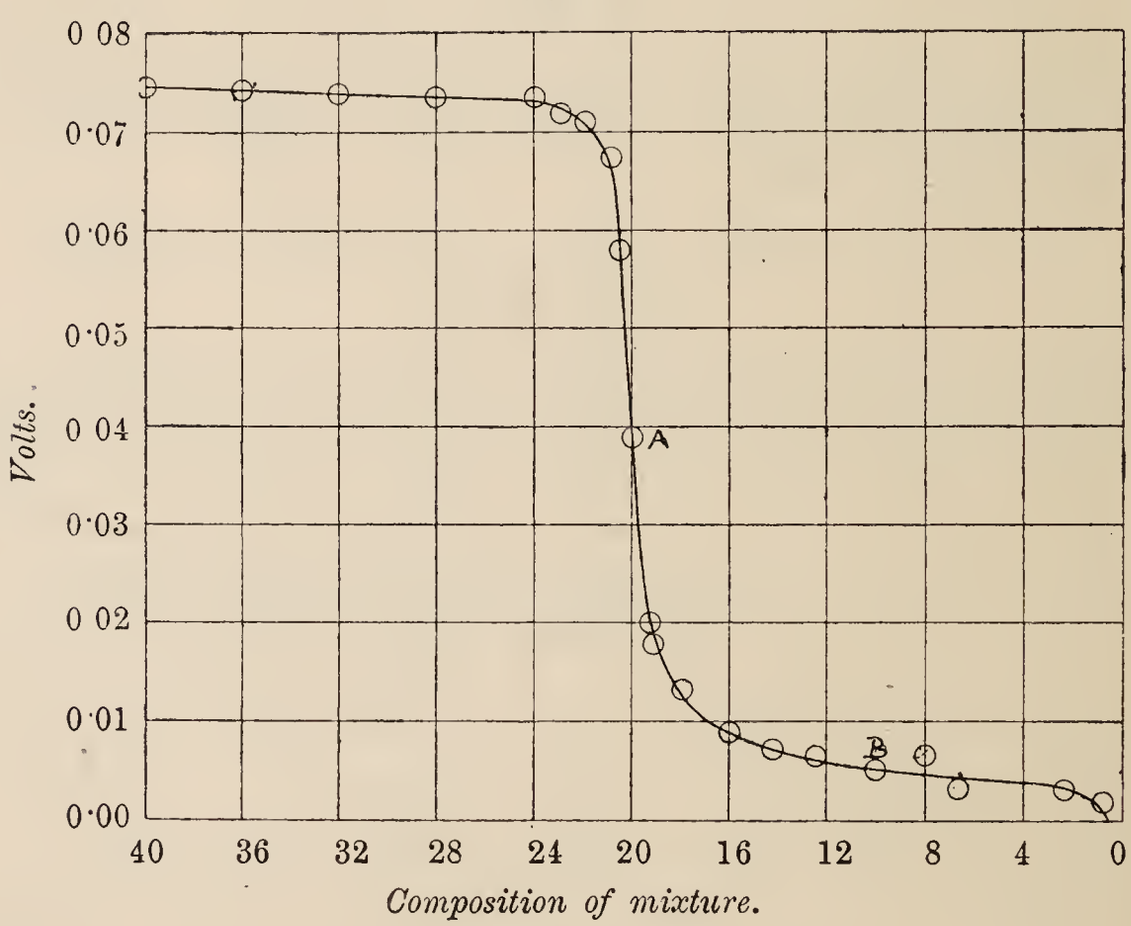
solutions dealt with in this paper increases with dilution. In Fig. 2 a curve is plotted demonstrating the relationship between

FIG. 1.



the change of *E.M.F.* on dilution and the composition of the mixture diluted. Within a fraction of a millivolt the right-hand

FIG. 2.



half of this curve serves for both series. As ordinates are plotted the change of *E.M.F.* on twenty-fold dilution, and, as abscissæ, numbers representing, as in Fig. 1, the composition of the solutions

in question. Points *A* and *B*, representing the change of *E.M.F.*, corrected for diffusion potential, on twenty-fold dilution, of 0·20*N*-acetic acid and "standard acetate" respectively, have been determined with the highest possible accuracy, using special electrodes and a silica electrode vessel. These form part of a series of determinations to be published in a later paper.

It will be seen that the rough statement that the hydrogen potential of acetic acid–acetate mixtures is independent of dilution holds rigidly for only one particular acetic acid–acetate mixture, and is, with the exception of solutions approximating in composition to pure sodium acetate, more nearly correct for solutions that are more alkaline than those which are more acid than "standard acetate."

The Electrometric Standardisation of Sodium Acetate.

If 20 c.c. of *N*-hydrochloric acid and 20 c.c. of *N*-sodium acetate are mixed, an error of 1 in 1000 in the relative strengths of the hydrochloric acid and sodium acetate solutions, or in the measurement of either, would produce an error of 0·94 millivolt in the potential reading of a hydrogen electrode in equilibrium with the solution. Now this mixture, if the measurement of the liquids is theoretically exact, is a solution which is 0·20*N* with respect to both sodium chloride and acetic acid. In spite of its sensitiveness to strong acids, and the salts of strong bases and weak acids, it can be reproduced readily with great exactness from pure *N*-sodium chloride and *N*-acetic acid, and, moreover, since

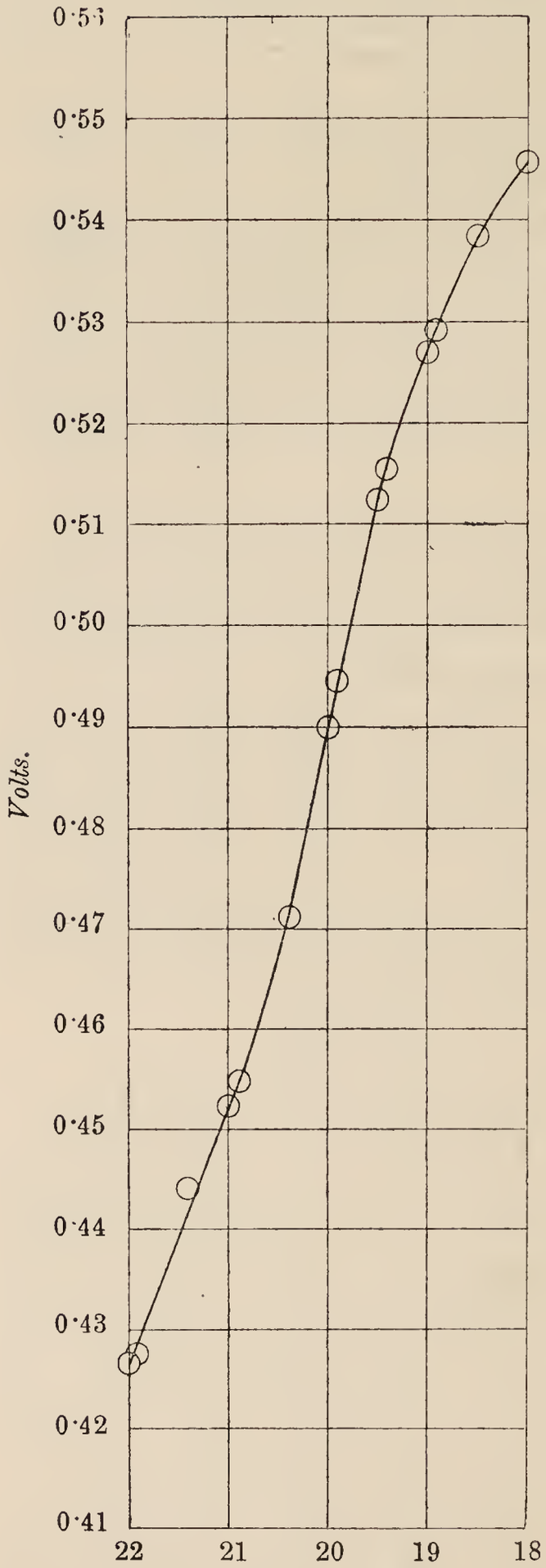
$$[H^{\cdot}] = \sqrt{k_a[HAc]} = \sqrt{k_a(C - [H^{\cdot}])},$$

a slight error in the concentration of the acetic acid will have a still smaller effect on the hydrion concentration of the solution.

These facts have been made the basis of the method employed to prepare *N*-sodium acetate solution. I have adopted the definition: "Normal sodium acetate solution is a solution of pure sodium acetate of such concentration that when 20 c.c. are taken, mixed with 20 c.c. of *N*-hydrochloric acid, and diluted to 100 c.c., the potential of a hydrogen electrode in equilibrium with it is the same as that of a hydrogen electrode in equilibrium with a solution 0·20 normal with respect to both acetic acid and sodium chloride."

To facilitate the preparation of normal sodium acetate in accordance with this definition a small part of the lower curve of Fig. 1 is reproduced in Fig. 3 on a different scale. The *E.M.F.* values have been taken, however, from column 6, and not column 8, and are therefore the direct results obtained against the decinormal electrode when the connecting fluid is saturated potassium chloride solution. The rapid change of *E.M.F.* with the composition of the

FIG. 3.



C.c. N-*Hydrochloric acid added to* 20 *c.c. of* N-*sodium acetate and diluted to* 100 *c.c.*

solution in the neighbourhood of "20 c.c. of *N*-hydrochloric acid + 20 c.c. of *N*-sodium acetate diluted to 100 c.c." is at once apparent. The curve is here a straight line, and the correction for 1 per cent. error in adjustment of the two solutions is 9·4 millivolts.

To illustrate the method employed to determine the exact concentration of an approximately normal sodium acetate solution an actual example may be given.

Twenty c.c. of *N*-hydrochloric acid were mixed with 20 c.c. of the sodium acetate solution to be standardised, and the mixture diluted to 100 c.c. This diluted solution gave, in equilibrium with a hydrogen electrode, 0·4800 volt against a 0·10*N*-calomel electrode.

Referring to the curve, it is seen that the ratio

$$\frac{\text{(concentration of hydrochloric acid)}}{\text{(concentration of sodium acetate)}}$$

is 20·20/20·00. Hence the concentration of the sodium acetate solution is 0·9901*N*, and in use, whenever a certain volume, say, x c.c., of 1·000*N* sodium acetate are required there must be measured out x c.c. of this solution, plus x c.c. of the same solution 100 times diluted.

As consecutive differential measurements of this *E.M.F.* may be made readily, with certain accuracy to a fraction of a millivolt. this method of standardising sodium acetate solution

may be trusted to the extreme limits of precision of volumetric measurement as ordinarily applied.

Throughout all the determinations in this work the normal standard acetate solution used was adjusted to an accuracy of 1 in 1000 in accordance with the electrometric definition given above.

The Preparation of "Standard Acetate" Solution.

There are now available two methods of preparing "standard acetate."

(1) From *N*-sodium hydroxide solution free from carbon dioxide and *N*-acetic acid adjusted by a suitable titration (using phenolphthalein), so as to be exactly equivalent to it.

(2) From *N*-sodium acetate and *N*-acetic acid adjusted by a titration of a baryta solution (see p. 2501), the strength of which is known exactly in terms of the *N*-hydrochloric acid solution used to standardise electrometrically the normal solution of sodium acetate.

As the accuracy of the hydrion concentration of the "standard acetate" solution depends to a greater extent on the exact equivalence of the amounts of sodium acetate and acetic acid present than on their absolute amount, the relative accuracies with which *N*-hydrochloric acid and *N*-sodium hydroxide can be prepared is a question which does not enter into these considerations. There does not appear to be any evidence that either of the methods (1) or (2) above is the more accurate, although for the preparation of *N*-sodium acetate solution itself the second method is to be preferred.

In table I it is seen that the mean of the hydrogen potential measurements for C=0·08 and C=0·12 is within a tenth of a millivolt of the same value for C=0·10, that is, "standard acetate." In other words, the upper curve of Fig. 1, which represents these measurements, is, between these points, a straight line. Also, it will be shown in a later paper that the change of this potential resulting from a change of concentration of "standard acetate" solution in the ratio y is exactly $\log y/262{\cdot}1$ volts. Hence, if in an attempt to prepare "standard acetate" one solution be measured with theoretical accuracy and be of exact normal strength, and the other be x per cent. incorrect either in its standardisation or in its measurement, the difference of hydrogen potential in volts between the resulting sodium acetate–acetic acid mixture and that of the true "standard acetate" will be:

$$\frac{x}{20}(0{\cdot}6148-0{\cdot}6046)\pm\frac{1}{262{\cdot}1}\log\left(\frac{100+x/2}{100}\right).$$

The choice of algebraic sign, + or −, will depend on whether

the incorrectly measured solution is the sodium acetate or the acetic acid, and whether its strength is x per cent. greater than or x per cent. less than normal. In practice, however, the right-hand part of this expression may be ignored entirely, for even when $x=6$ its value only reaches 0·05 millivolt, and the statement made with all practical accuracy that an error of 1 per cent. made in the standardisation of either solution or its measurement will lead to an error of 0·51 millivolt in the hydrogen potential of the resultant "standard acetate," and the relationship between the percentage error in standardisation or measuring one of the solutions and the resultant potential error, is one of simple proportion.

In view of these remarks it is the more easy to accept the convincing experience that with either of the two methods described it is possible to reproduce "standard acetate" with great accuracy. The most searching hydrogen potential measurements can barely detect with certainty differences between different preparations of this solution. On this account and because of its very small contact potential (which connotes a negligible "time change") against potassium chloride solutions, Michaelis's recommendation of it as the most suitable solution for checking the working of hydrogen electrodes can be confirmed. It should, of course, be remembered that the N-acetic acid solution and the acetic acid from which the N-sodium acetate solution is made must be of known purity.

Summary.

The contact *E.M.F.* between acetic acid–sodium acetate mixtures and a potassium chloride solution is of the order of 0·10 millivolt. Hydrogen *E.M.F.* measurements, corrected for this small potential difference by Bjerrum's extrapolation method, have been made of a series of these mixtures against the 0·10N-calomel electrode. With these have been compared the calculated results obtained by the well-known energy relationship and Fels's original equation. By the introduction of three rational corrections to this equation, one of them based on the principle of isohydrism, calculated results have been obtained agreeing with those observed to within 1·5 millivolt or less over the whole range from pure acetic acid to a mixture containing thirty-two times as much sodium acetate as acetic acid. The original equation is less accurate than the new equation for solutions containing much sodium acetate, and is grossly inaccurate for mixtures approximating to pure acetic acid in composition. For pure acetic acid Fels's equation is indeterminate, whereas the new equation simplifies to the correct expression for the hydrion concentration of acetic acid in terms of its dissociation constant and its concentration.

A second series identical with the first, excepting only that sodium chloride was present in concentration equal to the acetic acid, has also been examined.

Determinations have also been made of the change of hydrogen potential of these series of solutions on twenty-fold dilution. The statement that the hydrogen potential of acetic acid–acetate mixtures is independent of dilution holds rigidly for only one particular acetic acid–acetate mixture, and is, with the exception of solutions approximating in composition to pure sodium acetate, more nearly correct for solutions that are more alkaline than those which are more acid than "standard acetate."

An electrometric method of standardising sodium acetate capable of development to a high order of accuracy has been devised and described. Using this method, the hydrogen electrode *E.M.F.* of the "standard acetate" solution of Michaelis can certainly be reproduced to within ±0·10 millivolt, and probably with even a higher order of accuracy.

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